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THE CALCAREOUS CONCRETIONS OF KETTLE POINT, LAMBTON COUNTY, ONTARIO

It cannot be said that the mechanics of the concretionary process in sedimentary rocks is well understood. The well-known spherical concretions of Kettle Point, at the southern end of Lake Huron, appear to throw some light on the problem of the *mise en place* of thoroughly exotic material, aggregated by this slowly acting molecular attraction. The purpose of the present paper is to illustrate the mode of occurrence and to indicate some facts leading toward the interpretation of these singular bodies.

Logan has given us a concise description of the conditions at Kettle Point in the *Geology of Canada*, published in 1863.[1] Reference is also made to them by Rominger;[2] but in neither case was actual illustration employed nor description given of perhaps the most remarkable characteristic of the concretions.

About one half mile eastward of Kettle Point the highway from the town of Thedford decends sharply on a remarkably well preserved sea cliff of the formerly expanded Lake Huron, to the level of a gently sloping bench, cut in part in the drift, in part in the shales which underlie all this portion of Lambton county. At the Point itself the shales are seen to be wasting very rapidly on the face of a modern cliff from six to fourteen feet high and a few hundreds of yards in length. This condition is highly favorable to the exposure of the concretions, and one could hardly ask for more ideal sections for the study of structural details in the bed rock.

According to Logan these beds represent the equivalent of the Genesee Shale in New York state, which bears concretions of the same nature as those under consideration.[3] Rominger put them in his "Black Shale" division of Michigan,[1] which C. E. Wright has called the "St. Clair Group."[2] The wide extent of these shales is further emphasized by their correlation with the important zone of the "Huron Shale" in Ohio.[3]

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[1] Pp. 387, 388.

[2] Rep. Geol. Sur. Michigan, Vol. III, 1873–1876, p. 67.

[3] Cf. Hall, Geology, Pt. IV, in the Nat. Hist. of New York, pp. 220 and 230.

At the Ontario locality the rock is argillaceous throughout, of a dark brownish-gray to black color, which is partly due to the strong impregnation of bituminous matter, so abundant as to make the rock inflammable. Fossils are not rare; indeed, there is a very striking exhibition of large specimens of *Calamites inornatus*, and of other plants, lying prostrate in the shale. In addition to the calcareous concretions there is a great abundance of concretions of iron pyrites, which are, however, always small, generally lenticular, with the greatest diameter under three

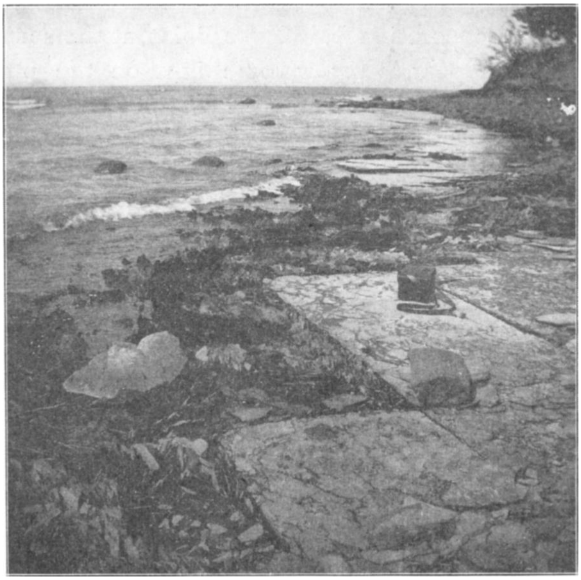

FIG. 1. General view of the shale at Kettle Point, showing jointing. Several concretions appear above the surface of the water.

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[1] Op. cit., p. 67.

[2] Rep. Geol. Sur. Michigan, Vol. V, 1881–1893, Pt. II, p. 21 (ed. by Lane).

[3] NEWBERRY, Geology of Ohio, Vol. I, 1873, p. 154.

inches. The decomposition of the pyrites has led to the efflorescence of the usual sulphates of iron and alumina and of the hydrous oxalate of iron, humboldtite.

The shale is nearly horizontal, well laminated and very fissile, the flakes of the rock being readily split out and piled up on edge by the waves, which thus build a curious belt of jagged and shattered fragments on the bed rock. The only other notable structure in the interconcretionary spaces is the universal occurrence of two extremely perfect systems of vertical joints at right angles to each other (Fig. 1). These joints affect the shale only, and do not pass through the concretions anywhere, so far as I have had opportunity of observing the latter.

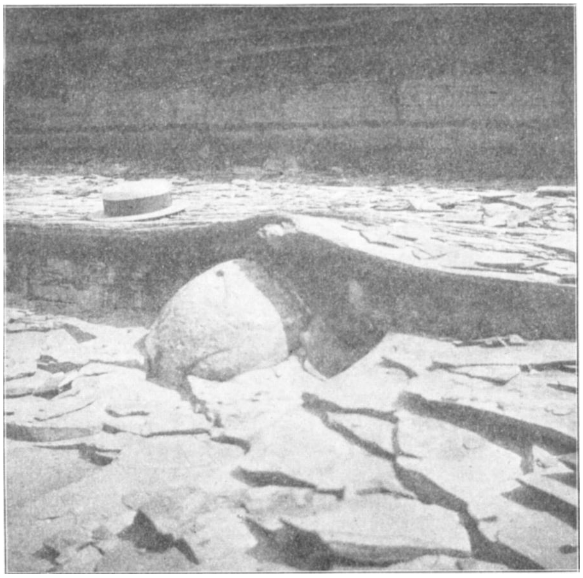

FIG. 2. Concretion and deformation of the shale.

The most striking structure in the shales is, however, the local departure from the normal horizontal position of the parts of the beds in the immediate vicinity of the concretions. In every one of the dozen well-exposed concretions still in place the strata are plainly arched over the upper hemisphere and bend under the lower, and show clearly the effect of deformation along the radii of the equator. In fact, the impression is at once given the observer that centrifugal force of nearly equal amount has been exerted along all radii of each sphere (Figs. 2, 3, and 5). A similar disturbance of the usual, nearly horizontal, attitude of the beds of this formation has been noted by Newberry at Worthington, Franklin county, Ohio,[1] and by Rominger in the "Black Shale" of Michigan.[2]

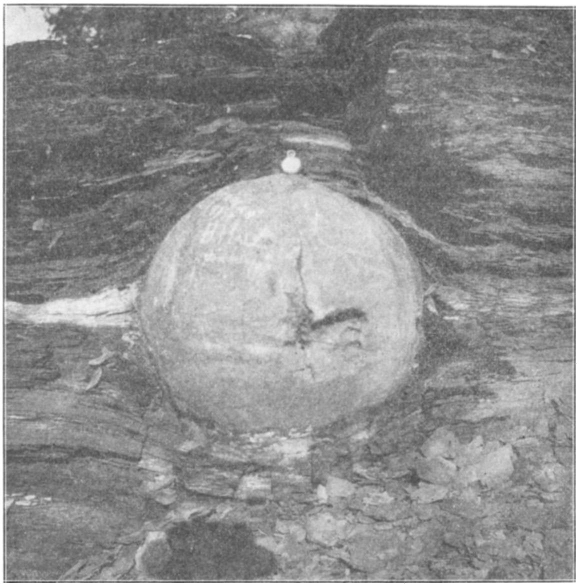

FIG. 3. Deformation of the shale about a medium-sized concretion.

The concretions themselves are composed essentially of crystallized carbonate of lime, the crystals arranged radially and always in direct contact with one another. There is practically no argillaceous material in them, and in no observed case does the stratification of the country-rock run through the concretion. The shape is usually that of the almost perfect sphere (Fig. 4), though often this form is somewhat lost by the slight flattening of the concretion along the diameter perpendicular to the plane of stratification of the shale. True spheres and spheroids exhaust the list of observed forms. The average diameter is nearly two feet; the largest specimen now well exposed on the shore, a spheroid, has a polar diameter of a little more than three feet, an equatorial diameter of about three feet six inches (Fig. 5); the smallest specimen may measure about one foot in diameter.

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[1] Geology of Ohio, Vol. I, 1873, p. 155.

[2] Op. cit., p. 66.

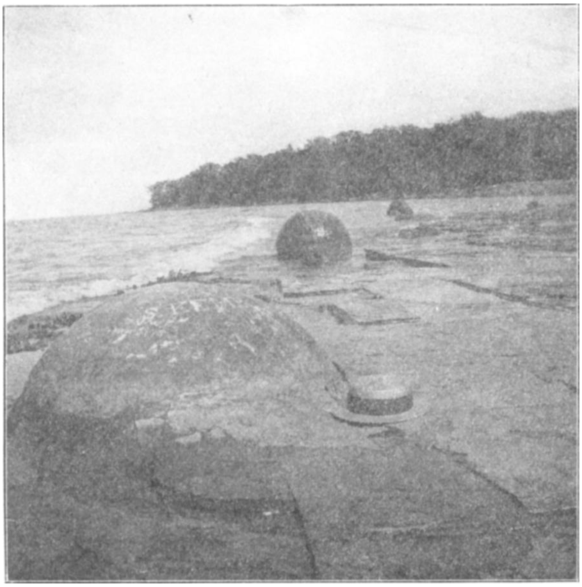

FIG. 4. General view of partially exposed concretions.

Large numbers of the concretions are being washed out of the much less resistant shales by the waves; their freeing from the matrix may be seen in all its stages (Fig. 4). But the number now remaining on the shore does not represent the total that could be counted were it not for the deplorable habit of the numerous visitors to the Point, who not only carry away the heavy specimens bodily, but break up others with the hope, destined to disappointment, of finding something at the core more interesting than the interior of the already shattered "kettles." It is said that the concretions may be seen on the bottom in the very shallow water of the lake five or six miles from Kettle Point, and that specimens may be readily fished from the bottom as much as two miles from the shore, where they have been leached out by the erosive action of the larger waves.

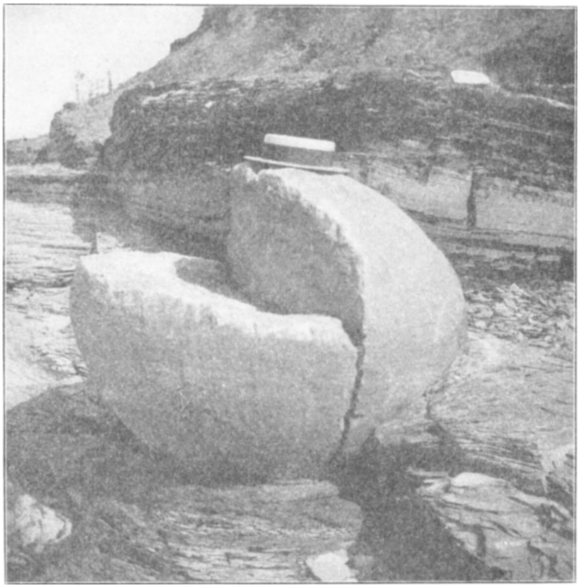

FIG. 5. Large concretion in place; the shale in its immediate vicinity exhibits slaty cleavage developed tangentially to the concretion.

Composing as they do such a comparatively large proportion of the rock, and occurring in similar profusion in the Upper Devonian of Michigan and Ohio, it is hardly just to say, in the words of Dana, that radial spherical concretions are "of inferior geological importance.[1]

A chemical analysis of one of the darker tinted brown concretions was made, and yielded the following percentage com position:

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[1] Manual of Geology, 4th ed., p. 97.

$CaCO_3$	88.42%
$MgCO_3$	2.99
Fe_2O_3	0.71
Residue insoluble in HCl (SiO_2)	4.25
Hydrocarbons (and H_2O)	3.23
	99.60

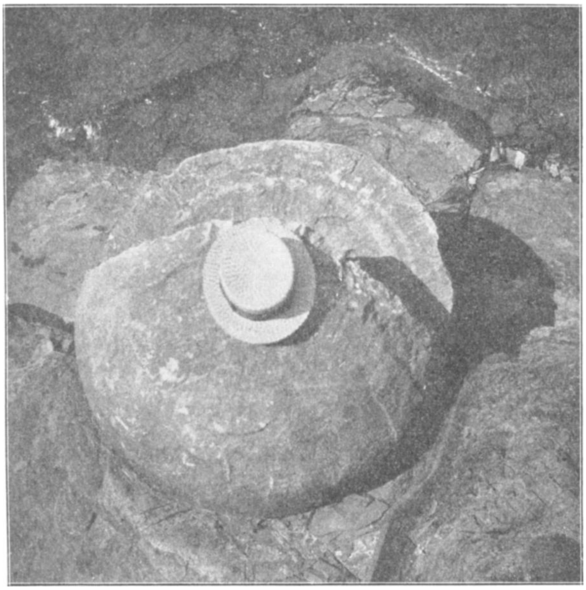

FIG. 6. Looking down on the concretion of Fig. 5; fractured surface shows concentric structure, the radial arrangement of the crystals not conspicuous in the photograph.

The powder from which this analysis was made was previously dried at ordinary temperatures in a desiccator; any residual water was driven off at the low heat used to expel the hydrocarbons. The latter cannot then be said to have been exactly determined, but they probably do not total less than 3 per cent. The shales round about were found by Hunt to contain 12.4 per cent. of volatile matter, presumably hydrocarbons.[1] The appearance of the magnesian carbonate is to be correlated with the observation by Garwood that some of this substance must be present if a limestone concretion is to grow large, although his analyses show that more than 30 per cent. of that carbonate seems to prevent the concretionary process.[1]

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[1] Chemical and Geological Essays, p. 179.

In all cases the structure is typically radial throughout the concretion, except at the rather indefinite small core of massive crystallized lime carbonate, which can usually be seen at the center. I have found no organic center of concretion, and no center other than calcite in any specimen. The free ends of the radiating crystals present the characteristic cleavage-planes of calcite, and the curved surface of the sphere is otherwise indented only by the faint depressions where the latter was in contact with the layers of shale (Fig. 5). Lastly, there is often to be seen, in addition to the radial structure, a concentric banding in the split-open sphere, a layering that seems to be original and connected with varying conditions of growth (Fig. 6).

The most important problem in connection with these concretions doubtless adheres to the question as to how the strata came to be deformed on all sides of each spheroid. That very considerable mechanical energy has been expended in the process is evident, not only in the development of a dome over the upper hemisphere and of a cup holding the lower hemisphere, but also in that of a sort of slaty cleavage, which can sometimes be discerned in the shale adjacent to the equatorial zone (Fig. 5). What is the source of the energy?

One of the first explanations that suggested themselves to me consisted in referring the deformation of the beds to differential movements in the strata as these adjusted themselves to the loss of water, and to the ensuing consolidation of the original muds to shale. The concretion itself would not lose bulk in such a case, and the layers overlying would be supported at the upper pole of the spheroid, while there would be less and less of such support for the same strata along lines radiating from the pole in the horizontal plane, until a maximum of instability would be reached outside of the equatorial circle. Here there would be a maximum of collapse which means, in the end, a doming above the upper hemisphere. I have found that the same explanation had been brought forward by both Newberry[1] and by Rominger.[2] But it leaves out of account the structural cup, which holds the lower hemisphere, and which is just as well developed as the dome overhead (Fig. 3). Moreover, the existence of the concretion before the act of consolidation is not considered; yet we must believe that a theory of the deformation should be controlled by the recognition of the fact that many cubic feet of the shale must be displaced to permit of the growth of the larger concretions.[3] We know of no reactions by which replacement of argillaceous material by slow molecular interchange with carbonate of lime may take place, nor can we conceive of such large spherical and spheroidal cavities as those necessary for the segregation of the calcite as having antedated the segregation. The last supposition is particularly invalid, for, in any case, it would leave the radial structure unexplained.

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[1] Geol. Mag., 1891, p. 439.

The same objection may be made to the hypothesis that energy sufficient for the deformation of the strata might be forthcoming in the process of forming a pseudomorph of calcite after some other carbonate of greater density. Siderite does, indeed, occur in radially concretionary form in the Black Shale of Michigan.[4] But, while there might be an important increase of volume with the application of expansive energy analogous to that ensuing on the change from anhydrite to gypsum, we have still to account for the original displacement of the shale to make way for the siderite or other earlier carbonate itself. It may also be stated that the disturbance of the shale is visibly greater than is possible on a mere change of volume in the pseudomorphosing reaction.

There thus seems to be no escape from the conclusion that the crystallization of each concretion and the opening of the space in which it lies were contemporaneous processes ; the force used in deforming the beds must, in some way or other, be directly connected with the act of crystallization of the calcite.

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[1] Op. cit., p. 155.

[2] Op. cit., p. 66.

[3] NEWBERRY'S largest concretion of the sort here described, and occurring under similar conditions, measures 10 feet in diameter, giving a volume of more than 500 cubic feet. Geology of Ohio, 1873, p. 155.

[4] Geol. Surv., Mich., Vol. III, 1873–1876, p. 67.

The theory of this association that lies nearest to hand would explain it by deriving active mechanical energy from each crystal of calcite as it obtains new material at the outer extremity on the surface of the growing spheroid. This energy will, then, be that of a "live force," and will be directed centrifugally, forcing the shale to assume a position dependent on the relative rate of growth of the crystals in the bundle. If there be equal supply of carbonate in the surrounding matrix, the radiating crystals will grow at equal rates; the aggregate will be spherical, and the layers of shale will be forced to assume a corresponding position. A rate of supply more rapid along the plane of stratification than in a direction transverse to that plane would give a spheroid with a minimum diameter similarly transverse to the bedding, and a corresponding distortion of the shale mantle. In brief, this hypothesis calls for the production of a compressive force exerted on the surrounding medium by a growing crystal.

Bischof has said that "what we know of causes in the growth of crystals, we have learned in the chemical laboratory. This is our sole guide to a conception of crystallization in the mineral kingdom."[1] It must be confessed that the advocates of the theory of live force exerted by natural crystals have been few, and that almost all derive their whole argument from observations in the geological field, and not from those in the chemical laboratory. Unfortunately, too, many of the examples chosen by them cannot be taken as sure evidence of the exertion of such force by a crystal of a primary mineral, *i. e.*, one that has gathered its molecules, one by one, from a mother liquor, and that by virtue of the attraction of like molecule to like. And this is the case with our calcite molecule. With but few exceptions the argument for live force has been taken from the study of minerals like wavellite, natrolite, and other zeolites, gypsum, serpentine, talc, and other hydrous secondary minerals; possibly pseudomorphs in every case, and if so, of less density, and occupying greater volume than the parent mineral. Such swelling substance can exert active centrifugal force. But we have already noted the fact that this cause of crowding in rock-masses cannot aid us greatly in explaining the Kettle Point concretions.

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[1] Lehrbuch der chem. phys. Geologie, 2d ed., Band I, p. 140.

Basing his statement on such doubtful examples as those just mentioned, Bischof says: "Crystallization is a force which may be compared with that of the expansive force of heat."[2] On the other hand, he quotes Kopp, who opposed Duvernoy in his theory of a mechanical energy of crystallization by showing that a crystal of alum growing in a vessel never does so by accretion on the face upon which the crystal rests at the bottom of the vessel. Kopp thus concluded that the mechanical energy of crystallization must be very slight, if existent at all, in this case, of a crystal of exceptional rapidity of growth that cannot overcome its own trifling weight when immersed in the mother-liquor.[1]

At the same time, certain observers have noted instances where live force seems to have been exerted during growth by crystals or crystalline aggregates, which may not, or, indeed, certainly have not, been pseudomorphous derivatives from preexisting minerals. De La Bèche, speaking of crystalline concretions of selenite and of iron pyrites, stated his belief that, in these cases, chemical affinity was strong enough "to overcome the attraction of cohesion" in the matrix.[2] Dana's example of rifting of quartzite by the growth of a limonitic deposit, and the wedging asunder of parts of a tourmaline crystal by the crystallization of quartz in which the tourmaline lies embedded, are toó well known to need more than mention.[3] Similarly, Worthen's disjointed crinoids, the plates of which were gradually separated by the deposition of quartz between them, are cited by Dana as proving displacement by the force of crystallization. More recently, Professor Shaler has appealed to the hypothesis of tensional force to explain the opening of certain vein-fissures, the latter not being explicable by the usually accepted idea of open fissures.[1]

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[1] BISCHOF, Lehrbuch, Band I, p. 134.

[2] Researches in Theoretical Geology, 1834, p. 91.

[3] Manual of Geology, 4th ed., p. 138.

In certain of these cases, it may be agreed that the mechanical force expended seems to have been applied *pari passu* with the process of crystallization ; so far as I have been able to find direct statement of the mode of application, each writer signifies his belief that the crystal itself did the work of rifting or of crowding together. We have seen that what little experimentation has already been carried out so far, leaves this interpretation decidedly weakened. The question arises as to whether the energy is set free in the act of crystallization in ways other than in the form of a push exerted by the growing crystal. An answer has suggested itself to me, and I shall briefly outline it, without, I trust, seeming to imply that the idea is anything more than a somewhat highly specialized working hypothesis.

In the Kettle Point shales, saturation of the underground waters by both free and combined carbon dioxide is not hard to imagine. An abundant supply of the gas could be found in the decomposition of the carbonaceous matter in the shales ;[2] the monocarbonate of lime is supplied in all necessary quantity from the calcareous bands in the shale and from the underlying Devonian limestones.

Suppose now that a small fragment of carbonate of lime, organic or other, is enclosed in a rock, with a capillary film between mineral and rock. This fragment will act as the immediate stimulus to the decomposition of any sufficiently saturated

[1] Bull. Geol. Soc. Amer., 1899, Vol. X, p. 259.

[2] The analysis of the gas given off from the "east crater" among the Mississippi mud-lumps of 1871 gave the following result: CO_2 9.41 per cent., marsh gas 86.20 per cent., N 4.39 per cent. HILGARD, Amer. Jour. Science, 1871, (1) p. 426. While the percentage of CO_2 is high, we may still regard this analysis as representative of the normal gases given off in the decomposition of vegetable matter buried in mud.

bicarbonated water that may be in contact with it.[1] Monocarbonate is precipitated about the fragment and a double biproduct is formed of water less strongly charged with the bicarbonate than before, and of carbon dioxide, which may be kept in solution in the water. The volume of new monocarbonate, together with that of the biproducts, is greater than that of the original bicarbonate;[2] expansion is necessary. The result would be the development of pressure directed centrifugally with respect to the fragment. This pressure will be the sum of all those minor pressures produced by the single decompositions of bicarbonated water entering by each of a million passages to the point where the solid carbonate is reached. The integrated force may have great efficiency. It would tend to expel the water from the surrounding capillary passages. If the expulsion kept pace with the crystallization, the space between the mineral and the adjacent rock-substance would soon be completely closed and crystallization and growth of the concretion would cease.

But the experiments of Jamin[3] have proved that equilibrium may exist between two unequal pressures affecting the ends of a capillary tube, provided a column of liquid occupying the tube be interrupted by bubbles of air. The presence of the latter excites capillary attraction which is so strong as to take up several atmospheres of pressure applied at one end of the tube. The force so expended is represented in the compression of the air bubbles and in changing the form of the air menisci; surface tension is thus overcome. The movement of the bubbles progressively decreases in the direction of the greater pressure until one is reached which is not disturbed at all so long as the pressures remain constant. The bubbles act like so many buffers. Any capillary tube filled with water interrupted by any insoluble gas or liquid possessing a lower surface tension than water, will exhibit the same phenomenon. Let us return to our incipient concretion.

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[1] It is a familiar fact that crystallization can often be brought about, when not produced by other means, by introducing a crystal of the substance, the crystallizing of which is desired. Further, the mass of substance dissolved in water and coming in contact with a mineral, is very small compared with that of the mineral; if there ensue a chemical reaction, it is the large mass of the mineral that regulates the laws of affinity. Thus, solid carbonate of barium decomposes dissolved bicarbonate of calcium, and solid calcium carbonate decomposes dissolved barium carbonate; à fortiori, solid calcium carbonate will decompose dissolved calcium carbonate, i. e., the bicarbonate. Cf. BISCHOF, Lehrbuch, Band I, p. 114.

[2] That expansion will result has unfortunately not yet been proved by experiment in the case of $CaCO_3$, but it is inferred from the law that expansion of volume follows on the separation of salts from their solutions in those instances where increased pressure aids solubility. Engel has determined that the solubility of carbonate of lime in carbonated water increases very rapidly with an increase of pressure, e. g., doubling with a rise of pressure from one to six atmospheres. Comptes Rendus, Vol. CI, p. 949.

[3] Comptes Rendus, Tome L, 1860, pp. 172 and 311.

Round about the grain of carbonate, there is an infinite network of capillary passages largely occupied by water in the early history of the rock. Along with the water, are gaseous and liquid hydrocarbons that are slowly being evolved by the decomposition of organic matter. The distribution of the hydrocarbons will be such as to bring about capillary attraction, and therewith the possibility of differential pressures within the water-mass, though it be in equilibrium throughout. Thus at the capillary film separating lime fragment and argillaceous wall, we may have great outward pressure unaccompanied by the expulsion of water along the channels leading from the country rock to the fragment. The latter is girt about with a mesh of capillary passages enormously resistant to movement of the contained liquids, and permitting of greater hydrostatic pressure within than without. The form of the mesh itself may change however, without interfering with its function as a buffer. The centrifugal pressure will then be occupied in deforming the rock, and it may conceivably be aided by the expansive energy of the freed CO_2. Fresh supplies of bicarbonated water will slowly diffuse into the capillary space between concretion and rock and further the displacing process. The solid carbonate as it were, keeps pulling a trigger that sets off the reaction of decomposition, which does not occur at a distance from the fragment. The biproduct cannot escape as fast as formed and the country-rock must be crowded away. The deformation is then, analogous to that produced by the freezing of water in a closed vessel, being caused by a change of volume, and not by the thrust of the crystals as such.

Much of this general scheme can be applied with certainty to the Kettle Point concretions. Bicarbonated water unquestionably was the source of the calcite substance; the decomposition was induced locally at the call of pre-existent carbonate, and the double biproduct described must have resulted. Since the joints in the shale are undoubtedly due to desiccation, it is but fair to suppose that the concretions antedate them. The presence of hydrocarbons during the concretionary growth is likewise reasonable. The resulting surface tension in this deep-lying water would thus bring about capillary action which was especially powerful on account of the extremely small size of the channels through which water could migrate in the shale.

The shape of the growing concretions will depend primarily on the resistances offered to displacement by the shale, and, perhaps, secondarily, to the rate of supply of bicarbonate. From the homogeneous character of the shale, we are led to believe that both of these actions will be nearly equal in all directions throughout the rock, with, however, a slight advantage in power of resistance to be ascribed to the direction at right angles to the plane of stratification. The resulting form of the concretions would, in consequence, be that of a sphere or of a spheroid. The calcite crystals will assume radial positions according to a law of crystal growth that does not concern us here; they will grow outward into the shallow space offered by the outward thrust until the biproduct has slowly diffused through the argillaceous wall.

In conclusion, then, it may be stated that the concretions were formed in place within the shale, that they antedate the period of joint development and final consolidation of the surrounding rock, that the local deformation of the shale accompanied the process of crystallization, and that the energy of the deformation appears to have been derived from the change of volume induced by the breaking up of the bicarbonate into monocarbonate and fluid biproduct. The introduction of capillarity to explain the existence of differential pressures in the rock-mass cannot be regarded as other than hypothetical. It is hoped that the suggestion may lead to fruitful experimentation; for it is doubtless to the experimental geologist and to the physical chemist that we must finally appeal in determining the source of mechanical energy in deep-seated chemical reactions. The hypothesis should, of course, also be tested by reference to the conditions at other localities where deformation in sedimentary rocks has been produced during the growth of concretions, whether composed of calcite or of other material.

REGINALD A. DALY.